

Thermomechanical treatment method for Fe-Mn-Si-based
shape memory alloy with Nb, C addition

TECHNICAL FIELD

5 The present invention relates to a thermomechanical treatment method for a Fe-Mn-Si-based shape memory alloy with Nb, C addition. More particularly, the present invention relates to a thermomechanical treatment method for a Fe-Mn-Si-based
10 shape memory alloy with Nb, C addition which exhibits a satisfactory shape memory effect without undergoing so-called training, providing improved performance.

BACKGROUND OF THE INVENTION

15 It has been a long time since the Fe-Mn-Si-based shape memory alloys had been proposed and invented. However, unfortunately, the alloys of Fe-Mn-Si system may be currently in a situation that the alloys are not sufficiently used yet and not yet put to practical use.
20 The main cause is that the alloys can not exhibit satisfactory shape memory effect without undergoing a special thermomechanical treatment called training.

 Here, the training means a process sequence of repeating the following treatment several times to
25 improve shape memory effect. The treatment consists of deforming an alloy by 2-3% at room temperature and then heating it to around 600°C higher than the reverse transformation temperature of the alloy.

In the face of the situation of prior art in which the aforementioned troublesome training is indispensable, inventors of this invention have earnestly studied aiming at developing a treatment with simple process, especially not requiring the training. As a result, the inventors have found a fact that if a small amount of Nb and C elements is applied to a particular shape memory alloy i.e. a Fe-Mn-Si-based shape memory alloy and a suitable aging heating treatment is subjected to the alloy to generate fine NbC carbides in structure of the alloy, a sufficiently satisfactory shape memory effect is obtained without undergoing the troublesome treatment called training, and thus previously filed a patent application (see Patent Document 1). The inventors have studied also about the thermomechanical treatments for the alloy with Nb, C addition, and they found a fact that pre-deformation in a temperature range of from 500°C to 800°C and a subsequent aging treatment lead to a further improved shape memory effect and thus also filed patent applications about this (see Patent Document 2, Patent Document 3).

Patent Document 1;

Japanese Patent Unexamined Publication No. 2001-226747

Patent Document 2;

Japanese Patent Unexamined Publication No. 2001-296901

Patent Document 3;

Japanese Patent Unexamined Publication No. 2002-79295

We believe that the inventions proposed in the
aforementioned prior applications facilitate astonishing
progress in the shape memory alloy technology,
5 contribute to put the shape memory alloy to practical
use for the future, and greatly contribute to the
development of industry. However, there are still some
points to be improved in proposed inventions. As for the
two latter prior applications (Patent Document 2, Patent
10 Document 3), the inventions proposed in these
applications are significantly meaningful because the
"quite easy treatment process is achieved as well as
further improved shape memory performance of alloy. In
addition, it was recognized that the shape memory
15 performance is therefore dramatically improved, thus
dramatically increasing the degree of practical use.
That is, the works and effects of the inventions of
these applications are quite noticeable. However, there
still remains a problem that the treatment process
20 requires a heating treatment in a high temperature range
of from 500°C to 800°C, which causes difficulties in
most cases. It is undeniable that this point makes it
difficult to put the shape memory alloys to practical
use.

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DISCLOSURE OF THE INVENTION

The object of the present invention is to
fundamentally solve the aforementioned problems.

The inventors of this invention has earnestly studied aiming at developing and ensuring good shape memory properties for a shape memory alloy of specified components even with deformation at low temperatures. As
5 a result, they found that the satisfactory shape memory properties can be sufficiently ensured even with deformation at room temperature so as to achieve the aforementioned object.

That is, they found amazing fact that the
10 excellent shape memory property of alloy can be developed just by applying a basic operation comprising deforming a Fe-Mn-Si-based shape memory alloy with Nb, C addition at room temperature and then subjecting the deformed alloy to aging heating treatment to precipitate NbC
15 carbides. In brief, the aforementioned object is achieved by the present invention.

The present invention was made on the basis of the aforementioned knowledge and success. The solving means to solve the problems are the followings (1)-(7).

20 (1) A thermomechanical treatment method for a Fe-Mn-Si-based shape memory alloy with Nb, C addition comprising: deforming a Fe-Mn-Si-based shape memory alloy with Nb, C addition by a deformation ratio of from 5% to 40% at room temperature, and subjecting the
25 deformed alloy to aging treatment to precipitate NbC carbides.

(2) A thermomechanical treatment method for a Fe-Mn-Si-based shape memory alloy with Nb, C addition

according to the above (1), wherein the Fe-Mn-Si-based shape memory alloy with Nb, C addition comprises, as alloy components, Mn: 15% to 40% by weight, Si: 3% to 15% by weight, Nb: 0.1% to 1.5% by weight, C: 0.01% to 0.2% by weight, and Fe and inevitable impurities: residual amount, wherein the atomic ratio Nb/C between Nb and C is 1 or more.

(3) A thermomechanical treatment method for a Fe-Mn-Si-based shape memory alloy with Nb, C addition according to the above (1), wherein the Fe-Mn-Si-based shape memory alloy with Nb, C addition comprises, as alloy components, Mn: 15% to 40% by weight, Si: 3% to 15% by weight, Cr: 1% to 20% by weight, Nb: 0.1% to 1.5% by weight, C: 0.01% to 0.2% by weight, and Fe and inevitable impurities: residual amount, wherein the atomic ratio Nb/C between Nb and C is 1 or more.

(4) A thermomechanical treatment method for a Fe-Mn-Si-based shape memory alloy with Nb, C addition according to the above (1), wherein the Fe-Mn-Si-based shape memory alloy with Nb, C addition comprises, as alloy components, Mn: 15% to 40% by weight, Si: 3% to 15% by weight, Cr: 1% to 20% by weight, Ni: 0.1% to 20% by weight, Nb: 0.1% to 1.5% by weight, C: 0.01% to 0.2% by weight, and Fe and inevitable impurities: residual amount, wherein the atomic ratio Nb/C between Nb and C is 1 or more.

(5) A thermomechanical treatment method for a Fe-Mn-Si-based shape memory alloy with Nb, C addition

according to any one of the above (2) through (4), wherein the atomic ratio between Nb and C is set in a range of from 1.0 to 1.2.

(6) A thermomechanical treatment method for a Fe-Mn-Si-based shape memory alloy with Nb, C addition according to any one of the above (2) through (5), wherein the Fe-Mn-Si-based shape memory alloy with Nb, C addition contains, as impurities, Cu: 3% by weight or less, Mo: 2% by weight or less, Al: 10% by weight or less, Co: 30% by weight or less, and/or N: 5000 ppm or less.

(7) A thermomechanical treatment method for a Fe-Mn-Si-based shape memory alloy with Nb, C addition according to any one of the above (1) through (6), wherein the conditions for the aging treatment are a temperature range of 400°C to 1000°C and an aging time from 1 minute to 2 hours.

EFFECT OF THE INVENTION

As a thermomechanical treatment for a Fe-Mn-Si-based shape memory alloy having specified components with Nb, C addition, "conventionally, the processing treatment" prior to aging is carried out by training. Alternatively, in the inventions of the prior applications, the processing treatment prior to aging is carried out in a temperature range of from 500°C to 800°C. According to the present invention, however, the processing treatment prior to the aging treatment can be

successfully carried out without high temperature, i.e. at room temperature, by setting a processing ratio in a specified range.

The technical meaning of the present invention must be clearly understood as compared to the prior art and the inventions of the prior applications on which the present invention is based because there are obvious difference therebetween. That is, according to the present invention, the remarkable improvement in shape memory property is achieved first time by a combination of specified alloy components, specified deformation ratio at room temperature, and setting of aging condition to a certain range. Amazingly by run-of-the-mill thermomechanical treatment comprising a deformation at room temperature and then aging, the shape recovery ratio equivalent to that of the sample subjected to the training can be obtained and, in addition, the shape recovery stress significantly larger than that of the sample subjected to the training can be obtained. With development of the present invention, it is expected that the use of shape memory alloys will be accelerated toward the practical use in a wide variety of fields.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagram showing relations between the amount of initial deformation and the shape recovery ratio depending on the thermomechanical treatment of Fe-Mn-Si-based shape memory alloys with Nb, C addition of

the present invention; and

Fig. 2 is a diagram showing the relation between the recovered shape strain and shape recovery stress depending on the thermomechanical treatment of Fe-Mn-Si-based shape memory alloys with Nb, C addition of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

The reason why the deformation ratio at room temperature is specified to be from 5% to 40% comes from the fact that the deformation ratio lower than 5% does not effectively contribute to improvement in shape memory property while the deformation ratio over 40% makes a sample too hard so that it is extremely difficult to deform the sample after subjected to an aging treatment.

An alloy as to be subjected to the thermomechanical treatment method for a Fe-Mn-Si-based shape memory alloy with Nb, C addition of the present invention has the following chemical compositions, just as specified in the prior applications, 1) Mn: 15% to 40% by weight, Si: 3% to 15% by weight, Nb: 0.1% to 1.5% by weight, C: 0.01% to 0.2% by weight, and Fe and inevitable impurities: residual amount, wherein the atomic ratio Nb/C between Nb and C is 1 or more;

2) The Fe-Mn-Si-based shape memory alloy with Nb, C addition has the following compositions Mn: 15% to 40% by weight, Si: 3% to 15% by weight, Cr: 1% to 20% by

weight, Nb: 0.1% to 1.5% by weight, C: 0.01% to 0.2% by weight, and Fe and inevitable impurities: residual amount, wherein the atomic ratio Nb/C between Nb and C is 1 or more; [] has the following compositions Mn: 15%
5 to 40% by weight, Si: 3% to 15% by weight, Cr: 1% to 20% by weight, Ni: 0.1% to 20% by weight, Nb: 0.1% to 1.5% by weight, C: 0.01% to 0.2% by weight, and Fe and inevitable impurities: residual amount, wherein the atomic ratio Nb/C between Nb and C is 1 or more.

10 In either of the Fe-Mn-Si-based shape memory alloys with Nb, C addition, the atomic ratio Nb/C between Nb and C in the alloy is preferably from 1.0 to 1.2.

Further, the alloy as to be subjected to a
15 thermomechanical treatment method for the Fe-Mn-Si-based shape memory alloy of the present invention is permitted to contain, as impurities, one or more of a group consisting of Cu of 3% by weight or less, Mo of 2% by weight or less, Al of 10% by weight or less, Co of 30%
20 by weight or less, and N of 5000 ppm or less.

Embodiments of the invention

Hereinafter, the invention will be specifically described on the basis of Fig. 1 and Fig. 2. It should
25 be noted that examples shown in the drawings are for the purpose of disclosure for helping the easy understanding of the present invention and are not intended to limit the scope of the present invention.

EXAMPLES

First, a Fe-28Mn-6Si-5Cr-0.53Nb-0.06C alloy (% by weight) with Nb, C addition of the present invention was prepared by melting. How the shape memory property is improved by rolling at room temperature and then subjecting it to an aging treatment in a temperature range of 400°C to 1000°C for a time period from 1 minute to 2 hours, is shown below.

FIG. 1 is a graph showing differences in shape recovery ratio among a case in which only aging was conducted (0% rolling) and cases in which aging was conducted after rolling by 10%, 20% and 30% at room temperature. In all of the cases, the aging treatment was conducted at 800°C for 10 minutes. For comparison, results of samples of the Fe-28Mn-6Si-5Cr alloy with no Nb, C addition prepared only by annealing and samples of the alloy prepared after subjected to the training five times are shown. The abscissa shows the initial strain (%) by tensile deformation at room temperature, and the ordinate shows the recovery ratio of strain when the sample is heated to 600°C. When heated to 400°C, approximately the same shape recovery ratio is also obtained. The samples used in tests were test pieces having a thickness of 0.6 mm, a width of 1 to 4 mm, and a length (gage length) of 15 mm.

As is known from this figure, the sample rolled by 10% has shape memory recovery ratios nearly equivalent

to or slightly lower than those of the alloy with no Nb, C addition which was subjected to training five times. Practically the necessary initial strain is believed to be about 4%. A shape memory recovery ratio of about 90%
5 shown at this strain strongly suggests that it is used as a practically applicable alloy. Training of at least five times is necessary for obtaining the same shape recovery ratio as this sample, with a conventional Fe-Mn-Si-based shape memory alloy with no Nb, C addition.
10 As is understood from this, the present invention exhibits shape memory properties with a simple method.

The sample with a higher rolling ratio of 20% has shape memory recovery ratios nearly equivalent to or slightly higher than those of the case without rolling
15 (only aged). However, the sample with a further higher rolling ratio of 30% has shape memory recovery ratios lower than those of the case which was only aged in a range with large initial strain.

On the other hand, as for shape recovery stress
20 which is one of the important shape memory properties for practical use, the shape recovery stresses of samples aged after rolling by 20% and 30% are remarkably improved. Fig. 2 is a graph showing the degrees of improvement in shape recovery stress of these samples,
25 in comparison with the case in which only aging was conducted (0% rolling) and a case in which the aging was conducted after rolling by 10%. The recovery stress when recovered strain on the abscissa is zero means the

stress generated when a sample is tensile-deformed at room temperature, then, heated to the reverse transformation temperature or more in a state that the both ends of the sample are fixed without any recovery, and returned to room temperature again. The recovery stress at recovered strain of 2%, for example, means the stress generated in case that the both ends of the sample are fixed after a recovery of strain by 2%. Tests were conducted with the initial strain given at room temperature of from 4% to 6%.

The test pieces used were the same as those used for obtaining the results shown in Fig. 1. The recovered strain on the abscissa in Fig. 2 is explained, taking a case where a shape memory alloy is used as a coupling for examples. It is equivalent to the ratio (%) of clearance between the pipes and the coupling part (shape memory alloy) to the diameter. Remarkable increase in shape recovery stress is observed in a range of high rolling ratio: a shape recovery stress of 310MPa is obtained at the recovered strain of 0% when the rolling ratio is from 20% to 30% at room temperature and a shape recovery stress of 200 MPa is obtained even at the recovered strain of 2% for the same rolling ratio. It is also found that the same shape recovery stress as the case subjected to training is obtained even in a case that the rolling ratio is 10%.

That is, as is known from the results of this figure (Fig. 2), remarkable increase in shape recovery

stress is observed in cases of high rolling ratios (20%, 30%) as compared to the cases of a rolling ratio of 0% and a rolling ratio of 10%. For the sake of comparison, Fig. 2 shows shape recovery stresss of the sample with
5 no Nb, C addition and the sample subjected to the training five times. It is seem from this figure that the recovery stresses of these samples are much smaller than those of the present invention.

As described above, the present invention was made
10 by finding that the deformation treatment prior to the aging treatment to a Fe-Mn-Si-based shape memory alloy having specified components with Nb, C addition can be successfully carried out at room temperature if the deformation ratio is in a specified range. The technical
15 meaning of the present invention must be clearly understood because there are obvious advantages as compared to a conventional one which requires the training accompanied by troublesome operation and the inventions of the prior applications which still require
20 high-temperature deformation in a range of from 500°C to 800°C.

That is, according to the present invention, the remarkable improvement in shape memory property is achieved first time by a combination of specified alloy
25 components, specified deformation ratio at room temperature, and setting of aging condition to a certain range. Amazingly by run-of-the-mill thermomechanical treatment comprising a deformation at room temperature

and then aging, the shape recovery ratio equivalent to that of the sample subjected to the training can be obtained and, in addition, the shape recovery stress significantly larger than that of the sample subjected to the training can be obtained. Anyway, the meaning of the present invention is significant. The shape memory alloy according to the present invention can be used as tightening materials for various applications, for example, for tightening water pipes, tightening oil pipes, etc., which will produce great economic effects.

It should be noted that the applications as tightening materials mentioned above are just examples and the present invention is not limited to such applications. With the development of the present invention, it is expected that the shape memory alloy will be put to practical use for various applications in a wide variety of fields.

INDUSTRIAL APPLICABILITY

The present invention provides a thermomechanical treatment means for a Fe-Mn-Si-based shape memory alloy having specified components with Nb, C addition with simple processing treatment prior to aging. Conventionally, the processing treatment prior to aging is carried out by training. Alternatively, in the inventions of the prior applications, the processing treatment prior to aging is carried out in a temperature range of from 500°C to 800°C. According to the present

invention, however, the processing treatment prior to the aging treatment can be successfully carried out without high temperature, i.e. at room temperature, if using a processing ratio in a specified range.

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10 improvement in shape memory property is achieved first time by a combination of specified alloy components, specified processing ratio at room temperature, and setting of aging condition into a certain range.

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20 time by a combination of specified alloy components, specified deformation ratio at room temperature, and setting of aging condition to a certain range. Amazingly by run-of-the-mill thermomechanical treatment comprising a deformation at room temperature and then aging, the
25 shape recovery ratio equivalent to that of the sample subjected to the training can be obtained and, in addition, the shape recovery stress significantly larger than that of the sample subjected to the training can be

obtained. With development of the present invention, it is expected that the use of shape memory alloys will be accelerated toward the practical use in a wide variety of fields.